# Anomalous temperature dependence of the resistivity of single-wall carbon nanotubes

Antonis N. Andriotis*

*Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, P.O. Box 1527,
71110 Heraklio, Crete, Greece*

Madhu Menon[†]

*Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky 40506-0055
and Center for Computational Sciences, University of Kentucky, Lexington, Kentucky 40506-0045*

George E. Froudakis

*Department of Chemistry, University of Crete, P.O. Box 1470, 71409 Heraklio, Greece*

(Received 17 February 2000)

The anomalous behavior of conductivity observed in experiment of single-wall carbon nanotubes is shown to be due to the effects of residual transition metal catalysts residing in close contact with the nanotube walls. A combination of analysis of the density of states based on the tight-binding molecular dynamics and a simple model calculation provides a good description of the resistivity behavior observed in experiment.

Single-wall carbon nanotubes (SWNT's) are metallic or nonmetallic depending on their chirality. Among the many exotic properties observed for the nanotube is the anomalous behavior of conductivity as a function of temperature. The reported experimental data for the resistance, $R$, of the ''armchair'' SWNT (either in the form of SWNT mats or SWNT bundles or even in the form of a single nanotube) indicate a shallow minimum at a temperature $T = T^\star \approx 40$–$300$ K. For $T > T^\star$, the metallic SWNT's exhibit a positive $dR/dT$, which is characteristic of metallic behavior.[1] For $T < T^\star$, however, $dR/dT$ is negative. Various mechanisms have been proposed to explain this anomalous $R(T)$ behavior. Fischer *et al.*,[1] note that the measured values of the SWNT diameters and resistances satisfy the Thouless criterion for one-dimensional localization, suggesting that weak localization may be responsible for the observed anomaly in $R(T)$. Kaiser, Dusberg, and Roth,[2] on the other hand, noting the similarity between the resistivity behavior of SWNT's and that of the highly conducting polymers, suggested that the observed anomaly in $R(T)$ may be due to a possible mixing of metallic and disordered barrier regions that might have occurred during the formation of the SWNT. Other suggested mechanisms include the effect of inter-tube interactions within the bundle[3,4] and the presence of metallic and nonmetallic tubes in the sample.[3] Finally, Gregorian *et al.*,[5] observing that the transition metal (Fe, Ni, Co) catalysts reside in close contact with the nanotube walls, suggested that the Kondo type mechanism may be responsible for the observed $R(T)$ anomaly. It is worth noting that recent experimental results,[5] in contrast to earlier reports,[6] show that transition metal catalysts cannot be totally removed from the SWNT surfaces even after they are treated with annealing and argon bombardment.

In this work we provide a plausible explanation for the anomalous $R(T)$ behavior observed in experiments based on the detailed electronic structure analysis of SWNT with transition metal catalysts in contact. The stable geometries of various Ni chemisorption sites on SWNT were obtained using our tight-binding molecular dynamics (TBMD) method.[7] The scheme allows one to perform spin and geometry unrestricted energy minimization realistically for the determination of lowest energy structures. The method uses a minimal parameter basis set to obtain a transferable tight-binding parametrization of the Ni-Ni, C-C, and Ni-C interactions applicable to binary $Ni_m C_n$ systems. The data base for fitting the parameters is obtained from experimental and/or *ab initio* results for small $Ni_m$, $C_m$, and $Ni_m C_n$, $n + m \leq 4$ clusters, the latter obtained using the density functional method and the coupled cluster method with single, double, and triple excitations.[7] This parametrization, incorporated into the tight-binding molecular dynamics scheme, has been used with success to study $Ni_m C_n$ clusters of arbitrary sizes as well as the interaction of Ni with graphite[7] and the $C_{60}$ molecule.[8]

Our TBMD calculations have shown that curvature plays an important role in determining bonding sites for Ni on nanotubes.[9] In particular, only two distinct bonding sites were found to be stable for Ni chemisorbing on (5,5) and (10,10) ''arm-chair'' SWNT's. These consist of (i) The atop site, where the Ni atom bonds directly over a carbon atom while also forming additional bonds with the two nearest neighbor carbon atoms [Fig. 1(a)]. (ii) The bridge site, where the Ni atom resides over a C-C bond [Fig. 1(b)]. Due to the strong Ni-C interactions, the chemisorption of Ni results in considerable distortions in the SWNT. The atop site was found to be energetically more favorable.

Additionally, we also performed *ab initio* calculations with the GAUSSIAN 98 program package,[10] and the ONIOM method[11] to separate the cluster configuration obtained by the TBMD calculations into two segments. The first segment contained the Ni atom with 13 nearest C atoms forming three connected hexagons, treated using fully *ab initio* (B3LYP/LanL2DZ) method. The second segment contained the remaining cluster of C atoms and treated using molecular mechanics method. The *ab initio* calculations yielded an energy difference of 0.21 eV between these two adsorption sites.
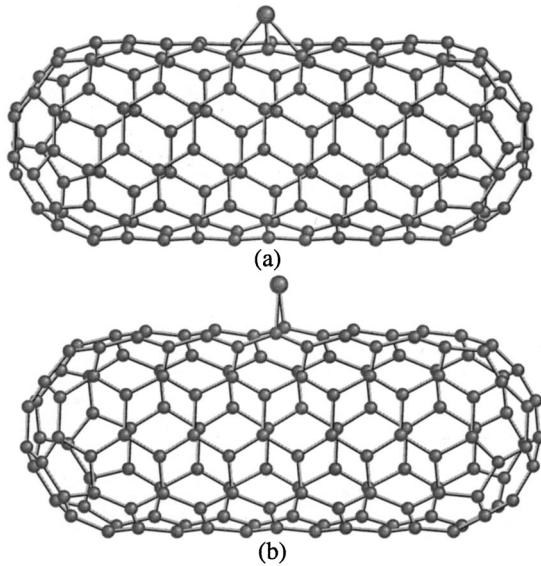
FIG. 1. The two stable binding sites for a single Ni on a (5,5) carbon nanotube wall; (a) atop site and (b) bridge site.

The TBMD results for the magnetic moment of the adsorbed Ni atom, its charge state and its bond lengths with the neighboring carbon atoms at these two adsorption sites are presented in Table I. A comparison of similar calculations for Ni on graphite revealed qualitatively different results.[9]

Interestingly, in addition to the anomalous $R(T)$ behavior, the experimental results also show a strong variation of the crossover temperature $T^{\star}$ among samples of SWNT prepared from the same doped target.[1] Furthermore, the temperature dependence of the resistivity (the resistivity increase at low $T$) (Ref. 1) is found to be reminiscent of Kondo alloys, and may point to spin-flip scattering from traces of Ni and Co incorporated into the SWNT. In this case, it is worth noting that $T^{\star}$ also provides a measure of the magnetic impurity density in Kondo alloys.

With these experimental facts at hand, we focus our efforts on the effects of Ni atoms on the SWNT with a view to provide us with an explanation of the issues raised by the experiments.

In Figs. 2(a) and 2(b) we present the changes in the electron density of states (DOS) that the Ni atom induces in the electron DOS of the SWNT upon its adsorption at the atop and bridge sites, respectively.[12,13] These figures have been obtained by subtracting from the electron DOS of the Ni-tube system the electron DOS of the tube in the absence of the Ni atom while keeping the tube at its relaxed geometry.[14]

TABLE I. Summary of results for Ni on a nanotube wall. Positive values of charge transfer indicate *loss* of charge on Ni, while negative values indicate *gain* in charge on Ni. The values of the magnetic moment $\mu$ are in Bohr magnetons ($\mu_B$). The numbers in parentheses denote the number of times the given quantity is repeated.

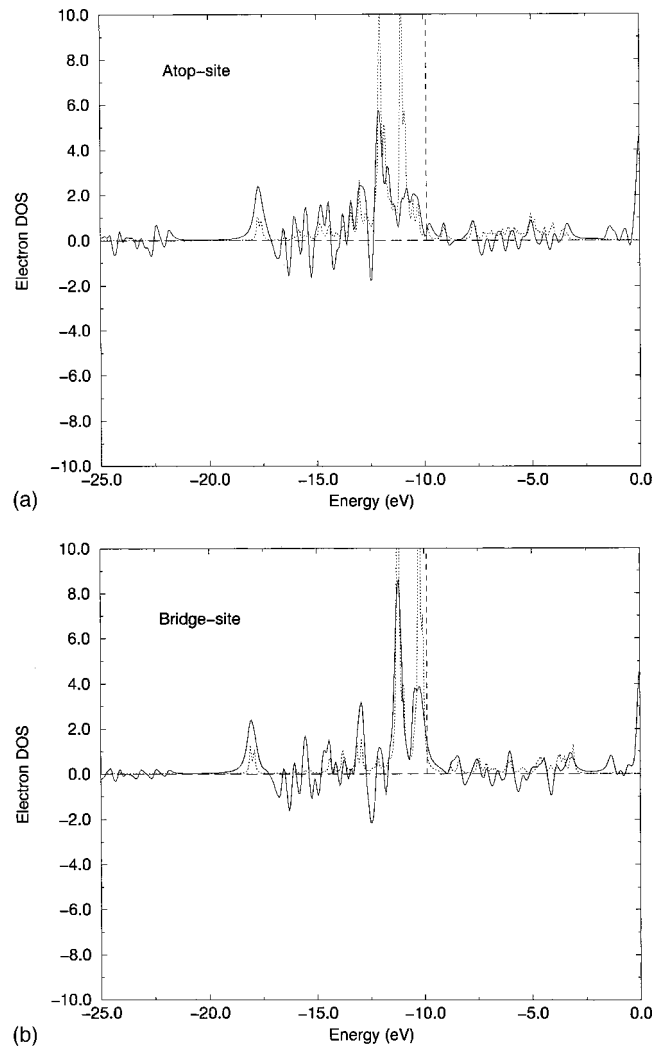| | Site | Charge transfer ($e$) | $\mu$ ($\mu_B$) | Ni-C bonds (Å) |
|---|---|---|---|---|
| Ni tube | atop | −0.05 | 0.15 | 1.79, 1.95 (2) |
| | bridge | −0.18 | 0.10 | 1.76 (2) |



FIG. 2. (a) The change in the electron DOS (solid curve) of the (5,5) single-wall carbon nanotube induced by the adsorption of a single Ni atom on an atop site. The LDOS at the Ni site is shown by the dotted curve. The Fermi energy is indicated by the vertical dashed line. (b) The same as for 2(a) for a Ni atom on a bridge site.

Also shown in the same figures are the local densities of states (LDOS) for the chemisorbed Ni atom (dotted lines). The most interesting feature that emerges from these figures is that for the Ni atom at the bridge site there is a substantial Ni contribution to the electron DOS of the Ni-SWNT system at the Fermi energy ($E_F$). Analysis of the LDOS reveals the contribution near $E_F$ coming almost entirely from the Ni $d$ orbitals. On the other hand, as can be seen in Fig. 2(a), for the Ni atom binding at an atop site, the Ni contribution to the electron DOS at the Fermi level is substantially less. We also performed $\rho(E_F)$ calculations for Ni positions in the vicinity of the stable positions obtained for atop and bridge sites. Our calculations show that appreciable value of $\rho(E_F)$ is attained only very near the bridge site. Furthermore, the results of Table I indicate no significant changes in the values of the magnetic moment of Ni at the atop and bridge sites.

Based on this information, we present a simple model calculation to provide an explanation for the anomalous behavior of the resistivity observed in the SWNT, namely its negative upturn with decreasing temperature.

Due to the metallic (or, more specifically, semimetallic) character of the (5,5) SWNT, its electron conductivity is well described by the expression:

$$\sigma = \frac{ne^2 \tau(E_F)}{m}, \qquad (1)$$

where $n$ is the electron density per unit volume, $m$ and $e$ the mass and the charge of the electron, respectively. $\tau(E_F)$ is the relaxation time evaluated at the Fermi energy $E_F$. A simple expression for the relaxation time indicates that[15]

$$\tau(E) \sim \frac{1}{T\rho(E)}, \qquad (2)$$

where $T$ denotes the temperature and $\rho(E)$ the electron DOS.

In addition to the bulk resistivity described by Eqs. (1) and (2), there is a substantial surface contribution induced by the adsorbed atoms of the catalyst (Ni,Co). This contribution is proportional to the electron DOS, and $\rho(E_F)$, and can be expressed as[16,17]

$$\chi_{surf} \cong \lambda \rho(E_F), \qquad (3)$$

where $\lambda$ is a temperature independent constant depending on the system characteristics $n$, $m$, $E_F$ and width of adsorbate resonance.

Equations (1)–(3) in combination with the results of Figs. 2(a) and 2(b) can be used to provide the following justification for the anomalous temperature dependence of the resistivity of the $(n,n)$-SWNT's: In the experiment reported, SWNT samples were produced by the laser ablation process and condensed on a water-cooled Cu surface.[1] These samples contain Ni and Co catalyst residues in close contact with the SWNT.[5] For Ni catalyst the only stable bonding geometries are the two shown in Fig. 1. Given the small energy difference between the two configurations, at low enough temperatures both sites are equally likely, having been trapped in local minima on annealing. As the temperature increases, however, Ni atoms may move (diffuse) from these sites to less stable ones depending on the activation energy barrier towards these states and the thermal energy of the Ni atoms.

According to our calculations, the occupancy of the atop site cannot be affected by temperature induced changes of the Ni position due to the sharp local energy minimum associated with this site. However, this does not appear to be the case for the bridge site which is found to be almost isoenergetic (within a range of 10 meV) with adjacent adsorption sites. It is therefore reasonable to assume that only the occupancy at bridge sites, $N_{bridge}(T)$, changes with temperature.

In order to explain the observed anomalous temperature dependence of the resistivity of the SWNT we invoke two competing mechanisms, one dominating at low and the other at high temperatures. Starting at low temperature, as $T$ increases, most of the bridge adsorption sites are gradually replaced by their nearest less stable ones. At these sites, our results indicate that the electron DOS at $E_F$ is smaller than that of the corresponding relaxed bridge site. Thus, during this process, there is a reduction in the electron DOS at the Fermi level approximately according to the results of Figs. 2(a) and 2(b). Assuming this reduction in DOS at $E_F$ to offset the linear increase in $T$ in Eq. (2), the relaxation time

will increase, resulting in a decrease in electron resistivity. This continues until the bridge site to less stable sites replacement process is complete and then the metallic, linear temperature behavior takes over, resulting in an upturn in the resistivity.

To provide a quantitative description of our arguments we assume that the occupancy at bridge sites, $N_{bridge}(T)$, changes with temperature according to the expression

$$N_{bridge}(T) = N_{bridge}(T=0)[1 - e^{-(\Delta E_{act}/k_B T)}], \qquad (4)$$

where $k_B$ is Boltzmann's constant and $\Delta E_{act}$ the activation energy for making the transition from bridge to the nearby less stable site. Under this assumption, it is straightforward to show that the total resistivity $\chi_{tot}$ of the tube in contact with catalyst atoms [as described by Eqs. (1)–(3)] takes the form

$$\chi_{tot} = (A + BT)(\Gamma - \Delta e^{-E_{act}/k_B T}), \qquad (5)$$

where $A$, $B$, $\Gamma$, and $\Delta$ are positive constants.

Equation (5) reduces to the form proposed by Fischer and collaborators[1] for the temperature dependence of the resistivity as obtained by fitting their experimental data. The exact determination of the constants of Eq. (5) depends on the concentration of the catalyst atoms and their distribution on bridge and atop sites at the beginning of the experimental measurements.

Although an accurate determination of the concentration of the catalyst atoms is not feasible, an approximate estimate can be obtained as follows: Assuming equal numbers of Ni atoms at atop and bridge sites initially, i.e., $N_{atop} = N_{bridge} = N_0$ and letting $\eta$ denote the ratio between the electron DOS of the atop site to that of the bridge site, Eq. (5) shows that the crossover temperature $T^\star$ is given by the relation:

$$T^\star = \frac{E_{act}\chi_{surf}(1-\eta)}{2\eta k_B \chi_{bulk}}, \qquad (6)$$

where $\chi_{bulk}$ denotes the bulk contribution to the tube resistivity. It is apparent from Eq. (6) that for $\eta = 1$, i.e., when there is no change in the electron DOS at the Fermi energy, consistent with our assumptions, no crossing temperature is predicted.

If it is further assumed that $T^\star = 100$ K, $\eta \in [0.1 - 0.2]$, and $E_{act}/k_B = 116$ K (i.e., for $E_{act} = 10$ meV), we obtain a value for the ratio

$$\mu = \frac{\chi_{surf}}{\chi_{bulk}} \qquad (7)$$

to be $\mu \approx 0.3$. Using these approximate values, the total resistivity of the tube, $\chi_{tot}$, is found to be

$$\chi_{tot} \approx 400\alpha N_0 \rho_{atop}(E_F), \qquad (8)$$

where $\alpha$ is a proportionality constant defined as

$$\chi_{bulk} = \alpha T \rho_{atop}(E_F). \qquad (9)$$

An approximate way for determining $\alpha\rho_{atop}(E_F)$ is to set it equal to the temperature derivative of the resistivity for $T > T^\star$. Thus, from values for the resistivity of the tube around $T = T^\star$ and its temperature gradient for $T > T^\star$ (as

those obtained from Ref. 1) we can obtain an estimate of $N_0$. The value of $N_0$ obtained corresponds approximately to 5 $\times 10^{12}$ Ni atoms per $cm^2$ of the tube surface.

A similar study with V atoms on a (5,5) ''arm-chair'' SWNT resulted in the following findings: The V atom exhibits stable adsorbed positions at atop and bridge sites, just as in the case of the Ni atom. Additionally, V atoms can also reside stably at hole sites (i.e., over the center of the hexagonal rings).[19] However, at none of these sites V atom introduces appreciable changes in $\rho(E_F)$ of the V-tube system, in contrast to the case of Ni adsorption. This leads us to speculate that the anomalous $R(T)$ behavior will not be seen in SWNT samples with V residues.

The strong dependence of the induced electron DOS on the kind of the adsorbed transition metal atom and on its adsorption site is supported by a very recent study of a SWNT-Cu nanocontact that we became aware of at the completion of our work. In particular, Kong, Han, and Ihm[18] found that there exists a remarkable difference in the electron DOS of a SWNT-Cu contact which depends on whether the adsorption site is the atop or the bridge one. The difference found is striking enough to result in a Cu-tube bond which exhibits ionic character at the atop site and covalent character at the bridge site. However, in the present case of the Ni adsorption, although $\rho(E_F)$ appears smaller in the atop case, no gap is found to develop at $E_F$ that can justify the anomalous $T$ behavior of the resistivity.

---

*Electronic address: andriot@iesl.forth.gr

†Electronic address: super250@pop.uky.edu

[1] J. E. Fischer, H. Dai, A. Thess, R. Lee, N. M. Hanjani, D. L. Dehaas, and R. E. Smalley, Phys. Rev. B **55**, R4921 (1997).

[2] A. B. Keiser, G. Dusberg, and S. Roth, Phys. Rev. B **57**, 1418 (1998).

[3] J. Hone *et al.*, Phys. Rev. Lett. **80**, 1042 (1998).

[4] P. Delaney, H. J. Choi, J. Ihm, S. G. Louie, and M. L. Cohen, Nature (London) **391**, 466 (1998).

[5] L. Grigorian, G. U. Sumanasekera, A. L. Loper, S. L. Fang, J. L. Allen, and P. C. Eklund, Phys. Rev. B **60**, R11 309 (1999).

[6] Y. H. Lee, S. G. Kim, and D. Tomanek, Phys. Rev. Lett. **78**, 2393 (1997).

[7] A. N. Andriotis, M. Menon, G. Froudakis, and J. E. Lowther, Chem. Phys. Lett. **301**, 503 (1999).

[8] A. N. Andriotis and M. Menon, Phys. Rev. B **60**, 4521 (1999).

[9] M. Menon, A. N. Andriotis, and G. E. Froudakis, Chem. Phys. Lett. **320**, 425 (2000).

[10] GAUSSIAN 98, Revision A.6, M. J. Frisch *et al.*, Gaussian, Inc.,
Pittsburgh PA, (1998).

[11] S. Humbel, S. Sieber, and K. Morokuma, J. Chem. Phys. **105**, 1959 (1996).

[12] The electron DOS is obtained according to the formula: $\rho(E) = A\Sigma_i \delta/[(E-\varepsilon_i)^2 + \delta^2]$, where $A$ is a normalization constant and $\delta = 0.2$ eV.

[13] The local electron DOS is obtained by projecting the Green's function $G(E) = [E - H + i\delta]^{-1}$ onto the set of the basis functions of the given atomic site; $\delta = 0.05$ eV was used.

[14] No appreciable dependence of $\rho(E_F)$ on the relaxation of the carbon atoms has been found.

[15] See, for example, A.H. Wilson, in *The Theory of Metals* (Cambridge University Press, Cambridge, England, 1965).

[16] B. N. J. Persson, Phys. Rev. B **44**, 3277 (1991).

[17] H. Ishida, Phys. Rev. B **54**, 10 905 (1996).

[18] K. Kong, S. Han, and J. Ihm, Phys. Rev. B **60**, 6074 (1999).

[19] Similar results for the relative strength of the various adsorption sites were reported for Cu on a SWNT (see Ref. 18).